Osmotic Pressure Measurements of Glucose Solutions at 10°, and 20°

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH A REQUIREMENT FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

BY

WALTER H. COOLIDGE

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Osmotic Pressure Measurements of Glucose Solutions at 10° and 20°

The Cells.[1]

The cells used in the following experiments are made of a mixture of equal parts of a fire clay from Dorsey, Maryland, and a ball clay from Edgar, Florida. The clays are elutriated separately in an inclined wooden trough divided into compartments and the finer constituents of the clays thus obtained are bolted through Nos. 10, 14, and 16 silk bolting cloth, the latter having 24,336 holes to the square inch. The bolted clay is allowed to subside and the water above it drawn off by means of a siphon. Most of the water remaining in the clay is removed by the method of "electrical endosmose," which is as follows: A large porous pot is placed in a larger porcelain dish. The clay in the form of a thick porridge is poured into the pot and two electrodes are inserted, the anode into the clay and the cathode into the water which collects in the outer vessel. More clay is introduced from time to time and the water in the outer dish is kept at a constant level by means of an automatic siphon. When so much water is removed that cracks begin to appear in the clay, it is packed down with a pestle. A fall in potential of 110 volts is employed.

After drying by heat the two clays are now mixed in equal proportions by weight in the following manner: Equal weights are sifted; the mixture is churned with water for several hours and bolted through Nos. 14 and 16 bolting cloth; the material is dried by "endosmose," as described above, and is kneaded to a putty on a plate glass surface. The clay is now tamped down in the steel cylindrical press and as much water as possible is forced out by means of a wrench. The press is then placed in the compressing apparatus and the clay subjected to a pressure of 20 tons upon each square inch of its surface. The first descent of the weight is accomplished in about 2 hours and the second in about 16

1. For a detailed description see H N. Morse ; Carnegie Publication, No 198.

hours. The same results may be secured by lighter weights and longer pressing, or heavier weights and shorter pressing. The clay cylinder is removed from the press and is cut to form on the lathe.

The cutting of the cells from the cylinders requires extreme care. The cell wall must not be weakened at any point by the pressure of the cutting tools because, when the cell is baked, shrinkage takes place and the shrinking material draws away from regions of weakness and cracks are developed. To avoid this the cutting tools must have the proper "clearance" and the cell must never "sag."

The cells are baked at the kilns of the Bennett Pottery Company at a temperature of about 1300 degrees, or between the melting points of Seger cones Nos. 8 and 9. After baking the cells are mounted on the lathe and ground with a carborundum wheel to fit the brass rings with which the manometers are attached and to fit the cones upon the ends of the manometers. The glaze used must have the same coefficient of expansion as the cell, otherwise "crazing" results. A mixture of silica and feldspar added to one of the glazes used by the potters upon white tableware satisfies the requirement, and at the present time the glazing as well as the baking is done at the potteries.

Cells, when manufactured as described, have three necessary characteristics: (1) Great and uniform strength of wall; (2) The absence of "air blisters"; (3) A very fine and perfectly uniform wall texture to insure the meeting of the anion and cation just within the inner mouths of the pores. The necessity of great strength of wall is obvious, as is the elimination of air blisters which cause the deposition of subsidiary membranes in the interior of the cell wall. The necessity of forming the membrane at the interior surface of the cell wall is evident because, if it be located within the wall, the solution near the membrane, owing to the slowness of diffusion, will be less concentrated than the solution within the cell proper and, as a result, it would not be possible to know the final concentration of any solution placed in the cell. If the pores were of such size that the anion and cation would meet on the inner surface of the cell wall, the membrane would lack strength and be easily ruptured. This latter condition is realized if the pores are too small, so that to fulfill condition (3) the wall texture must not be too fine or too coarse and must be perfectly uniform.

The Membranes.[2]

The first step toward the deposition of the membrane is the removal of air from the pores of the cell and its replacement by water. This is accomplished by electrolyzing dilute solutions of salts, the result of which is the transportation of a volume of water by the cation of the salt used. The salt chosen is lithium sulphate because it has been shown that "the volumes of water carried through the porous wall of a cell, under identical conditions, are inversely proportional to the relative velocities of the various cations divided by their respective valencies." A 0.005 normal solution is employed. The cell is filled with the solution and immersed in it as far as the glazed portion. The electrodes are of platinum, the one within the cell serving as the cathode. The water drawn into the cell is automatically removed by means of a siphon. The liquid thus obtained is mixed from time to time with the solution outside of the cell. When the water has been removed from the pores the cell is emptied, rinsed, soaked for a time in distilled water and then filled with and immersed in pure water, and the electrolysis resumed. When the conductivity has fallen to that of distilled water, the cell is ready for the deposition of the membrane.

The apparatus for the deposition of the membrane is as follows: The anode, in the form of a copper cylinder, is placed in an empty glass vessel, and within the cylinder is placed the cell which is closed by a rubber stopper containing a funnel with a stem reaching nearly to the bottom of the cell, a platinum cathode and an overflow tube. The cell and the glass vessel are filled with one-tenth normal solutions of potassium ferrocyanide and copper sulphate, and the circuit is closed. A voltage of 110 is used.

The resistance at first is high owing to the fact that in the beginning the cell wall is filled with nearly pure water, but it soon falls and then rises again as the formation of the membrane progresses. Within an hour or two the resistance reaches a maximum and then begins to fall probably owing to an accumulation of alkali within the membrane itself. To prevent this as far as possible during the electrolysis, the ferrocyanide is renewed every five minutes through the funnel. When the maximum resistance is reached the circuit is broken and the cell is allowed to soak for several days in thymol water, the water being frequently renewed. The thymol water is an effectual preventative against infection by "pencillium" which otherwise is liable to

2. Ibid.

attack the membranes and soon destroy them. After three days the membrane forming process is repeated and the maximum resistance on this occasion is generally higher than that attained in the first electrolysis. The cell is placed in water again for three days and the alternate "running" and "soaking" continued until a final maximum resistance is reached which can be forced no higher. The maximum resistance finally attained varies greatly with the temperature, but is generally over 100,000 ohms.

The cell is now ready to be set up for "seasoning" the membrane under pressure. The cell is set up with a concentrated solution of glucose to which a small amount of ferrocyanide is added which is isosmotic with respect to the copper sulphate dissolved in the thymol water in which the cell is to stand. After the contents of the cell are subjected to a considerable mechanical pressure, it is then placed in a constant temperature bath and allowed to come to equilibrium. Evidently the meniscus comes to rest at a point generally below the position it should have, showing that the membrane has probably broken under pressure and has been mended by the "membranogens." This would cause a dilution of the contents of the cell and explain the fact that the solution does not develop the full osmotic pressure of the original solution. Whatever the result of the trial the cell is emptied, rinsed and soaked for several days in thymol water. The membrane forming process is then repeated and the cell set up again under pressure. In this way the cell is developed in about a month's time so that it will register full osmotic pressure and in which solutions undergo no dilution.

The membrane is developed at the temperature at which it is to be used for the measurement of pressure, and this necessitates keeping all of the solutions that are to be used with it at temperature also. The much repeated "soaking" is of great benefit to the membrane and cannot be dispensed with. A possible explanation of this is that the water extracts any alkali in the membrane and enables it to retain its colloidal condition which is necessary for semi-permeability.

The membranes vary greatly as regards their speed in attaining equilibrium. Other things being equal, water passes more slowly through a membrane in a hard burned cell in which the pores are small than it does through a soft burned cell in which the pores are large. Again, the rate of passage of water through a membrane decreases with the latter's age and use. Electrolytes also render a membrane sluggish.

The Manometers.[3]

The manometers used for the measurement of osmotic pressure have a bore of about .6 millimeter and a calibrated portion that ranges from 400 to 500 millimeters. Tubes of small bore are used because: (1) Short columns of mercury are introduced into the upper ends of the manometers in order to protect the calibrated portion of the tubes when they are closed. If the bore is large, the mercury is often dislodged by the severe tapping to which the manometers are subjected; (2) When the small volume of gas contained in the manometers is compressed, there results but little dilution of the solution in the cell; (3) Small amounts of mercury are required by manometers of small bore. The disadvantages of using tubes of small bore are: (1) It is more difficult to deal with the meniscus in a narrow tube; (2) The capillary depression is large in small tubes; (3) The movements of the mercury are greatly affected by the presence of impurities.

The mercury used in the manometers is purified as follows: (1) It is filtered through paper, air is forced through it at boiling temperature and the mercury is filtered again; (2) It is distilled in a vacuum; (3) The distillate is passed in a fine stream 1,000 times through a solution containing 2 per cent. nitric acid and 2 per cent. mercurous nitrate; (4) The mercury is distilled again in a vacuum using a new still. The mercury thus purified retains its luster in the air and is highly satisfactory. The bore of the tubes should be uniform and circular throughout, but neither of these conditions is very seldom realized.

The first step in calibrating a manometer is to etch upon it two fine lines extending around the tube. These lines are called the "scratches" and all readings are referred to one or the other of them. No other graduation appears upon the manometer. The bore of the tube is now calibrated by setting a thread of mercury exactly end to end and determining its length until the thread has passed along the tube the entire distance between the two scratches. It is then run out of the tube and weighed. Afterwards the whole of the calibrated portion of the manometer is filled with mercury, which is also run out and weighed. The mean diameter of the bore is calculated from the length and weight of the long thread and from the observed length of the small thread in different parts of the tube a mean calibration unit

3. Ibid.

is derived and a curve of corrections made. Finally, a mean correction for the double meniscus is obtained from the weight and length of the long and short threads. "If we multiply the weight of the short thread by the number of times its length is contained in the long thread, i. e., by the number of times it was set end to end, and subtract the product from the weight of the long thread, the difference is the weight of the mercury which would be required to fill all the meniscus spaces which were left vacant in setting the short thread end to end along the tube. Converting this difference in weight into volume, and dividing by the number of settings less one, we obtain a mean correction for a double meniscus, which is the meniscus correction to be applied in all measurements of pressure since the nitrogen in the manometers is always included between two mercury columns."

The capillary depression of the manometer is then determined. It is filled with pure mercury and is connected to a glass tube, having an internal diameter of 35 millimetres, by means of a rubber tube filled with mercury and reinforced with tape. This side tube enables the manipulator to adjust the mercury in the tube under examination to any desired height. The arrangement is placed in a constant temperature bath and the difference in height between the mercury in the manometer and that in the side tube is noted at points a few millimetres apart along the whole of the calibrated portion of the manometer. From the observed data a capillary depression curve is constructed and used (1) in determining the volume of the manometer, and (2) in correcting its voluume under an unknown pressure.

Pure nitrogen is now introduced into the manometer, a little mercury is run in after it and the tube is sealed. The volume of the manometer is determined by placing it in a bath of constant temperature and subjecting it to many known pressures of low magnitude.

Connection between manometer and cell is made by means of a brass cone which is covered with rubber and through which pass the manometers and also a very small brass tube terminating in a large threaded head. The two are held in place by Wood's metal. The small tube allows some of the solution to escape from the cell, when desirable, after connection between the manometer and cell has been made. The cone is forced tightly down into the cell by means of a brass collar and nut, forming a tight joint after the brass tube is closed by means of a screw plug with washer.

Regulation of Temperature.[4]

The principle of temperature regulation is as follows: "If the water or air in a bath is made to pass rapidly (1) over a continuously cooled surface which is capable of reducing the temperature slightly below that which it is desired to maintain, then (2) over a heating surface which is more efficient than the cooled one, but which is under the control of the thermostat, and (3) again over the cooled surface, etc., it should be practicable to maintain in the bath any temperature for which the thermostat is set, and the constancy of the temperature should depend only on the sensitiveness of the thermostat and the rate of flow of the water or air. Moreover, any desired temperature can be maintained without regard to the temperature of the surrounding atmosphere, since the air about the bath must always aid in the work either of the cooling or of the heating surface."

Since a closed osmotic cell is in some respects analagous to a sensitive thermometer, accurate regulation of the bath is necessary in order to prevent "thermometer effects" which take place with fluctuation in temperature and which develop in the cell a condition of over or under pressure. These phenomena may be understood by stating (1) that the capacity of a closed cell is a fixed quantity; (2) that every change in volume of the cell contents, due to rise or fall in temperature, is followed by a passage of solvent through the membrane which changes the osmotic pressure of the solution; and (3) that the passage of the solvent through the membrane is a much slower process than the changes in volume of the solution in the cell with change in temperature.

The type of bath used in the present work is about six feet long, five feet high, and 22 inches wide, made of heavy white pine and built in two sections, the upper being the "air space," and the lower the water compartment, which projects 15 inches beyond the upper to allow the placing of the pumping mechanism. Both compartments are lined throughout with tinned copper and are separated by a stout brass plate. This plate rests on top of the water compartment on rubber packing and carries the two parallel copper troughs which extend down into the water compartment and into which the cells with their manometers are placed. The thermostat and thermometer also project into the water through holes in the brass plate, and are fixed tightly in place by means of corks.

From the above description it is seen that the water compart-

4. Ibid.

ment is effectually closed, and that the air space above will never become saturated with or even contain an appreciable amount of water vapor, no matter at what temperature the bath may be running. If such were not the case, when the insulating pads are removed from the glass door in order to read the manometers, moisture might condense on the inside of the glass and, as a result, would interfere with accurate readings by means of the cathetometer. The interior of the bath is reached through a door made of heavy plate glass and running downward. The top is high enough to avoid the necessity of raising it when the cells are placed in the bath.

The cooling system of the water compartment consists of a parallel series of pipes lying on the bottom of the compartment and through which hydrant water runs at constant pressure. The heating system consists of two copper cylinders within which are placed electric lamps and which extend down into the water. The water is constantly circulated by means of a pump first over the cooling surface, and then over the heating surface. The temperature of the air space is regulated independently of that of the water. The cooling surface is identical to that used in the water compartment except that the pipe system is placed at the top of the air space. The constant source of heat within the air space is a pair of shaded electric lamps placed directly before an electric fan which keeps the air in circulation.

The thermostats are of large volume and the liquid used is toluene with mercury for electrical contact, rendering them very sensitive. The contact of the platinum wire in both thermostats is spanned by an electric light which effectually prevents sparking. The capillary was, nevertheless, cleaned regularly, and both thermostats worked perfectly throughout the whole investigation. The thermometers were calibrated against standards from the U. S. Bureau of Standards. The constancy of temperature was in general very satisfactory. The maximum deviation observed for periods of six or seven days often less than $\pm$ 0.02 of a degree. The variation at other times was much greater, but in such cases was generally traceable to some other cause, though not always. At first some difficulty was experienced in obtaining a constant flow of hydrant water through the cooling systems, but the trouble was successfully overcome.

The Weight Normal System for Solutions.[5]

A short account of how Morse and Frazer were led to the adoption of the weight normal system is as follows: "Soon after beginning the measurements of the osmotic pressure of cane sugar under conditions which gave to the results a considerable degree of precision, it became apparent that the mass of the solvent plays a part which appears to have been unsuspected hitherto. We found—or appeared to discover—that a gram-molecular weight of the substance, dissolved in water and diluted to a litre volume, is not the normal standard for osmotic pressure. On the other hand, when we dissolved a gram-molecular weight of cane sugar (342.22 grams) in 1,000 grams of water, i. e., in that mass of the solvent which has the unit volume one litre at the temperature of maximum density, we found its osmotic pressure at about 20 degrees in quite close accord with the pressure which a gram-molecular weight of hydrogen would exert, at the same temperature, if its volume were reduced to one litre; i. e., to that volume which the unit mass of the solvent has at the temperature of greatest density."

Thus the change from volume normal to weight normal was made and now we always have the same mass of solvent coming into play, no matter what the concentration of the solution. We have, in other words, corrected experimentally for the b in the van der Waal's equation as applied to solutions $(p + \frac{a^2}{v})(v-b)=$ constant, in which b is the volume of the dissolved molecules. For this reason the glucose solutions used in this investigation have been prepared according to the weight normal system.

5. Ibid.

MEASUREMENTS

TABLE I.

0.1 Wt. normal solution. Expt. 1 at 20°. Cell I_6. Resistance, 110,000 ohms. Manometer 60. Calc. gas pressure, 2.39 atms. Time of setting up cell, Dec. 2, 1914. Initial pressure, 3.527 atms. Observed osmotic pressures:

Final Record.

Atms.	Atms.
Dec. 27, 2.339	Jan. 2, 2.429
28, 2.401	3, 2.427
29, 2.416	4, 2.431
30, 2.416	5, 2.420
31, 2.405	8, 2.412
	9, 2.410
	(11 days)

Mean osmotic pressure ..... 2.415 atms.
Corr. mean osmotic pressure ..... 2.485 atms.
Mean ratio of osmotic to gas pressure 1.039

TABLE II.

0.1 Wt. normal solution. Expt. 2 at 20°. Cell 4. Resistance, 183,000 ohms. Manometer 61. Calc. gas pressure, 2.39 atms. Time of setting up cell, Jan. 10, 1915. Initial pressure, 2.539 atms. Observed osmot. pressures:

Final Record.

Atms.	Atms.
Jan. 25, 2.41	Jan. 29, 2.418
26, 2.405	30, 2.41
27, 2.416	31, 2.421
28, 2.421	Feb. 1, 2.419
	(8 days)

Mean osmotic pressure ..... 2.415 atms.
Corr. mean osmotic pressure ..... 2.477 atms.
Mean ratio of osmotic to gas pressure 1.032
Mean ratio of Expts. 1 and 2 ..... 1.035

TABLE III.

0.1 Wt. normal solution. Expt. 1 at 10°. Cell 14. Resistance, 182,000 ohms. Manometer 60. Calc. gas pressure, 2.308 atms. Time of setting up cell, Jan. 18, 1915. Initial pressure, 2.34 atms. Observed osmotic pressures:

Final Record.

Atms.	Atms.
Jan. 24, 2.34	Jan. 30, 2.315
25, 2.345	31, 2.312
26, 2.325	Feb. 1, 2.327
27, 2.315	2, 2.322
28, 2.326	3, 2.322
29, 2.318	4, 2.310
	(12 days)

Mean osmotic pressure ..... 2.3231 atms.
Corr. mean osmotic pressure ..... 2.388 atms.
Mean ratio of osmotic to gas pressure 1.034

TABLE IV.

0.2 Wt. normal solution. Expt. 1 at 20°. Cell A_6. Resistance, 275,000 ohms. Manometer 40. Calc. gas pressure, 4.78 atms. Time of setting up cell, Nov. 10. 1914. Initial osmotic pressure, 5.731 atms. Observed osmotic pressures:

Final Record.

Atms.	Atms.
Nov. 22, 4.91	Nov. 26, 4.933
23, 4.932	27, 4.94
24, 4.925	28, 4.891
25, 4.904	Dec. 3, 4.922
	(8 days)

Mean osmotic pressure ..... 4.9188 atms.
Mean ratio of osmotic to gas pressure 1.0296

TABLE V.

0.2 Wt. normal solution. Expt. 2 at 20°. Cell X_8. Resistance, 157,000 ohms. Manometer 43. Calc. gas pressure, 4.78 atms. Time of setting up cell, Nov. 10, 1914. Initial pressure, 4.835 atms. Observed osmotic pressures:

Final Record.

Atms.	Atms.
Nov. 22, 4.97	Nov. 26, 4.877
23, 4.90	27, 4.885
24, 4.895	28, 4.889
25, 4.915	Dec. 3, 4.911
	4, 4.899
	(9 days)

Mean osmotic pressure .....4.8934 atms.
Corr. mean osmotic pressure .....4.940 atms.
Mean ratio of osmotic to gas pressure 1.033

TABLE VI.

0.2 Wt. normal solution. Expt. 3 at 20°. Cell 2. Resistance, 157,000 ohms. Manometer 40. Calc. gas pressure, 4.78 atms Time of setting up cell, Dec. 22, 1914. Initial pressure, 4.095 atms. Observed osmotic pressures:

Final Record.

Atms.	Atms.
Jan. 16, 4.792	Jan. 20, 4.80
17, 4.80	21, 4.79
18, 4.819	22, 4.783
19, 4.81	23, 4.794
	(8 days)

Mean osmotic pressure .....4.7985 atms.
Corr. mean osmotic pressure .....4.915 atms.
Mean ratio of osmotic to gas pressure 1.028
Mean ratio of Expts. 1, 2, and 3.....1.030

TABLE VII.

0.3 Wt. normal solution. Expt. 1 at 20°. Cell X_6. Resistance, 157,000 ohms. Manometer 44. Calc. gas pressure, 7.170 atms. Time of setting up cell, Jan. 13, 1915. Initial pressure, 7.68 atms. Observed osmotic pressures:

Final Record.

Atms.	Atms.
Jan. 20, 7.336	Jan. 28, 7.307
21, 7.351	29, 7.323
22, 7.353	30, 7.324
27, 7.304	31, 7.332
	Feb. 1, 7.349
	(10 days)

Mean osmotic pressure .....7.3358 atms.
Corr. mean osmotic pressure .....7.393 atms.
Mean ratio of osmotic to gas pressure 1.031

TABLE VIII.

0.3 Wt. normal solution. Expt. 2 at 20°. Cell 5. Resistance, 122,000 ohms. Manometer 44. Calc. gas pressure, 7.170 atms. Time of setting up cell, Feb. 8, 1915. Initial pressure, 8.327 atms. Observed osmotic pressures:

Final Record.

Atms.	Atms.
Feb. 15, 7.457	Feb. 20, 7.365
16, 7.344	21, 7.377
17, 7.355	22, 7.362
18, 7.277	23, 7.394
19, 7.313	24, 7.377
	(10 days)

Mean osmotic pressure .....7.360 atms.
Mean ratio of osmotic to gas pressure 1.026
Mean ratio of Expts. 1 and 2 .....1.028

TABLE IX.

0.4 Wt. normal solution. Expt. 1 at 20°. Cell D_6. Resistance, 122,000 ohms. Manometer 37. Calc. gas pressure, 9.56 atms. Time of setting up cell, Feb. 17, 1915. Initial pressure, 10.143 atms. Observed osmotic pressures:

Final Record.

Atms.	Atms.
Feb. 22, 9.717	Mar. 1, 9.635
23, 9.701	2, 9.655
24, 9.706	5, 9.596
26, 9.620	6, 9.616
27, 9.651	

Mean osmotic pressure .....9.6159 atms.
Mean ratio of osmotic to gas pressure 1.010

TABLE X.

0.4 Wt. normal solution. Expt. 2 at 20°. Cell 5. Resistance, 91,000 ohms. Manometer 37. Calc. gas pressure, 9.56 atms. Time of setting up cell, March 10, 1915. Initial pressure, 10.342 atms. Observed osmotic pressures:

Final Record.

Atms.	Atms.
Mar. 16, 9.637	Mar. 29, 9.693
17, 9.765	30, 9.580
18, 9.684	31, 9.600
24, 9.676	Apr. 1, 9.617
25, 9.622	2, 9.603
26, 9.581	3, 9.602

Mean osmotic pressure .....9.638 atms.
Corr. mean osmotic pressure .....9.734 atms.
Mean ratio of osmotic to gas pressure 1.018
Mean ratio of Expts. 1 and 2 .....1.014

TABLE XI.

0.5 Wt. normal solution. Expt. 1 at 20°. Cell 1. Resistance, 183,000 ohms. Manometer 30. Calc. gas pressure, 11.95 atms. Time of setting up cell, Jan. 15, 1915. Initial pressure, 13.103 atms. Observed osmotic pressures:

Final Record.

Atms.	Atms.
Jan. 20, 12.26	Jan. 28, 12.193
21, 12.27	29, 12.22
22, 12.216	30, 12.212
23, 12.181	31, 12.254
27, 12.156	Feb. 1, 12.278
	(10 days)

Mean osmotic pressure .....12.224 atms.
Mean ratio of osmotic to gas pressure 1.023

TABLE XII.

0.5 Wt. normal solution. Expt. 2 at 20°. Cell X_8. Resistance, 137,500 ohms. Manometer 30. Calc. gas pressure, 11.95 atms. Time of setting up cell, Feb. 17, 1915. Initial pressure, 12.582 atms. Observed osmotic pressures:

Final Record.

Atms.	Atms.
Feb. 25, 12.259	Mar. 3, 12.151
26, 12.237	4, 12.191
27, 12.146	5, 12.194
Mar. 1, 12.172	6, 12.183
2, 12.226	8, 12.196
	(10 days)

Mean osmotic pressure .....12.195 atms.
Mean ratio of osmotic to gas pressure 1.021

TABLE XIII.

0.5 Wt. normal solution. Expt. 3 at 20 . Cell 2. Resistance, 200,000 ohms. Manometer 44. Calc. gas pressure, 11.95 atms. Time of setting up cell, March 2, 1915. Initial pressure, 15.376 atms. Observed osmotic pressures:

Final Record.

Atms.	Atms.
Mar. 9, 12.371	Mar. 13, 12.370
10, 12.362	15, 12.455
11, 12.474	19, 12.229
12, 12.391	20, 12.211
	21, 12.206

Mean osmotic pressure .....12.3069 atms.
Mean ratio of osmotic to gas pressure 1.0298
Mean ratio of Expts. 1, 2, and 3 .....1.0246

TABLE XIV.

0.6 Wt. normal solution. Expt. 1 at 20°. Cell 4. Resistance, 137,500 ohms. Manometer 30. Calc. gas pressure, 14.337 atms. Time of setting up cell, Dec. 11, 1914. Initial pressure, 14.122 atms. Observed osmotic pressures:

Final Record.

Atms.	Atms.
Dec. 23, 14.751	Dec. 28, 14.710
24, 14.735	29, 14.735
25, 14.810	30, 14.747
26, 14.771	31, 14.732
27, 14.774	Jan. 3, 14.730
	4, 14.753
	(11 days)

Mean osmotic pressure .....14.754 atms
Corr. mean osmotic pressure .....14.851 atms.
Mean ratio of osmotic to gas pressure 1.035

TABLE XV.

0.6 Wt. normal solution. Expt. 2 at 20°. Cell J_6. Resistance, 183,000 ohms. Manometer 45. Calc. gas pressure, 14.339 atms. Time of setting up cell, March 2, 1915. Initial pressure, 15.763 atms. Observed osmotic pressures:

Final Record.

Atms.		Atms.
Mar. 8,	14.793	Mar. 13, 14.670
9,	14.649	14, 14.786
.. 10,	14.622	15, 14.876
11,	14.734	16, 14.845
12,	14.679	18, 14.778
		(10 days)

Mean osmotic pressure .....14.743 atms.
Mean ratio of osmotic to gas pressure 1.0281
Mean ratio of Expts. 1 and 2 .....1.031

TABLE XVI.

0.7 Wt. normal solution. Expt. 1 at 20°. Cell E_6. Resistance, 220,000 ohms. Manometer 42. Calc. gas pressure, 16.729 atms. Time of setting up cell, Nov. 5, 1914. Initial pressure, 17.864 atms. Observed osmotic pressures:

Final Record.

Atms.		Atms.
Nov. 20,	17.082	Nov. 25, 17.179
21,	17.271	26, 17.286
22,	16.960	27, 18.368
23,	17.133	28, 17.180
24,	17.259	30, 17.191
		31, 17.174
		(11 days)

Mean osmotic pressure .....17.2802 atms.
Mean ratio of osmotic to gas pressure 1.032

TABLE XVII.

0.7 Wt. normal solution. Expt. 2 at 20°. Cell 3. Resistance, 275,000 ohms. Manometer 30. Calc. gas pressure, 16.729 atms. Time of setting up cell, March 16, 1915. Initial pressure, 16.526 atms. Observed osmotic pressures:

Final Record.

Atms.	Atms.
Mar. 1, 17.069	Mar. 5, 17.147
2, 17.152	6, 17.105
3, 17.140	7, 17.245
4, 17.105	8, 17.137
	(8 days)

Mean osmotic pressure .....17.1375 atms.
Corr. mean osmotic pressure .....17.2711 atms.
Mean ratio of osmotic to gas pressure 1.032

TABLE XVIII.

0.8 Wt. normal solution. Expt. 1 at 20°. Cell 5. Resistance; 183,000 ohms. Manometer 44. Calc. gas pressure, 19.119 atms. Time of setting up cell, Oct. 31, 1914. Initial pressure, 19.753 atms. Observed osmotic pressures:

Final Record.

Atms.	Atms.
Nov. 12, 19.833	Nov. 19, 19.741
13, 19.898	20, 19.790
14, 19.811	25, 19.792
15, 20,006	26, 19.836
16, 19.886	27, 19.780
17, 19.836	28, 19.852
18, 19.670	30, 19.827
	Dec. 1, 19.731
	(15 days)

Mean osmotic pressure .....19.819 atms.
Corr. mean osmotic pressure .....19.6948 atms.
Mean ratio of osmotic to gas pressure 1.0301

TABLE XIX.

0.8 Wt. normal solution. Expt. 2 at 20°. Cell 5. Resistance, 122,000 ohms. Manometer 44. Calc. gas pressure, 19.119 atms. Time of setting up cell, Dec. 6, 1914. Initial pressure, 20.824 atms. Observed osmotic pressures:

Final Record.

Atms.	Atms.
Dec. 23, 19.769	Dec. 28, 19.883
24, 19.806	29, 19.801
.. 25, 19.853	30, 19.806
26, 19.723	31, 19.776
27, 19.379	Jan. 3, 19.915
	4, 19.887
	(11 days)

Mean osmotic pressure .....19.823 atms.
Mean ratio of osmotic to gas pressure 1.036

TABLE XX.

0.8 Wt. normal solution. Expt. 3 at 20°. Cell I. Resistance, 157,000 ohms. Manometer 41. Calc. gas pressure, 19.119 atms. Time of setting up cell, Dec. 18, 1914. Initial pressure, 21.463 atms. Observed osmotic pressures:

Final Record.

Atms.	Atms.
Dec. 30, 19.777	Jan. 5, 19.753
31, 19.777	6, 19.521
Jan. 3, 19.654	7, 19.759
4, 19.758	8, 19.734
	9, 19.760
	(9 days)

Mean osmotic pressure .....19.7114 atms.
Mean ratio of osmotic to gas pressure 1.038
Mean ratio of Expts. 1, 2, and 3 .....1.034

TABLE XXI.

0.9 Wt. normal solution. Expt. 1 at 20°. Cell D_6. Resistance, 157,000 ohms. Manometer 33. Calc. gas pressure, 22.509 atms. Time of setting up cell, Dec. 15, 1914. Initial pressure, 23.612 atms. Observed osmotic pressures:

Final Record.

Atms.	Atms.
Dec. 28, 22.032	Jan. 3, 22.078
29, 22.014	4, 22.091
30, 22.017	5, 22.095
Jan. 2, 22.078	6, 22.146
	7, 22.130
	(10 days)

Mean osmotic pressure ..... 22.0304 atms.
Mean ratio of osmotic to gas pressure 1.0265

TABLE XXII.

0.9 Wt. normal solution. Expt. 2 at 20°. Cell J_6. Resistance, 157,000 ohms. Manometer 37. Calc. gas pressure, 22.509 atms. Time of setting up cell, Dec. 21, 1914. Initial pressure, 23.058 atms. Observed osmotic pressures:

Final Record.

Atms.	Atms.
Dec. 29, 21.907	Jan. 5, 21.891
30, 21.840	6, 21.840
31, 21.849	7, 21.951
Jan. 4, 21.894	8, 21.883
	9, 21.879
	(9 days)

Mean osmotic pressure ..... 21.8815 atms.
Corr. mean osmotic pressure ..... 22.029 atms.
Mean ratio of osmotic to gas pressure 1.0242
Mean ratio of Expts 1 and 2 ..... 1.0253

TABLE XXIII.

1.0 Wt. normal solution. Expt. 1 at 20°. Cell 3. Resistance, 366,000 ohms. Manometer 37. Calc. gas pressure, 23,899 atms. Time of setting up cell, Oct. 24, 1914. Initial pressure, 23.226 atms. Observed osmotic pressures:

Final Record.

Atms.		Atms.
Nov. 28, 24.368	Dec.	4, 24.393
30, 24.390		5, 24.324
Dec. 1, 24.285		7, 24.428
2, 24.259		8, 24.346
3, 24.286		10, 24.373
		(10 days)

Mean osmotic pressure .....24.3442 atms.
Corr. mean osmotic pressure .....24.4886 atms.
Mean ratio of osmotic to gas pressure 1.0246

TABLE XXIV.

1.0 Wt. normal solution. Expt. 2 at 20°. Cell 3. Resistance, 220,000 ohms. Manometer 32. Calc. gas pressure, 23.899 atms. Time of setting up cell, Dec. 15, 1914. Initial pressure, 25.698 atms. Observed osmotic pressures:

Final Record.

Atms.		Atms.
Jan. 13, 24.375	Jan.	19, 24.530
15, 24.646		20, 24.381
16, 24.375		21, 24.512
18, 24.450		22, 24.489
		23, 24.510
		(10 days)

Mean osmotic pressure ....24.4699 atms.
Corr. mean osmotic pressure .....24.612 atms.
Mean ratio of osmotic to gas pressure 1.030
Mean ratio of Expts. 1 and 2 .....1.0273

DISCUSSION OF TABLES

Tables I to XXIV give a somewhat detailed account of each experiment. It should be pointed out that the theoretical gas pressures given in these tables are calculated by means of the equation PV = KT in which V is the volume of the solvent in the pure condition at 4 degrees Centigrade. It should be noted, also, that the value 0.00367 t has been employed in all calculations of pressure; hence in so far as this coefficient is incorrect for nitrogen gas at the higher pressures, a correction is still to be applied to the osmotic pressures recorded in the tables. Furthermore, the concentration of a few of the solutions was found to be slightly changed when the cells were taken down, and in such cases the ratios were corrected for the resulting dilution or concentration.

The mean ratio by concentrations of all 24 determinations is tabulated below, and compared with the corresponding value for 30°—50° as recorded by Dr. Holland and Mr. Musselman.

	0.1 N	0.2 N	0.3 N	0.4 N	0.5 N
10°	1.034				
20°	1.035	1.030	1.028	1.014	1.0246
30°—50°	1.000	1.001	1.001	.999	1.006
	0.6 N	0.7 N	0.8 N	0.9 N	1.0 N
20°	1.031	1.032	1.034	1.0253	1.0278
30°—50°	1.000	1.006	.999	1.000	1.000

CONCLUSION

The osmotic pressure of all concentrations of glucose solutions from 0.1 to 1.0 weight normal at 20°, and the 0.1 weight normal solution at 10°, has been shown to differ in a marked manner from the values that have been obtained from 30° to 50°. At the latter temperatures all concentrations obey the equation of Van't Hoff $PV = KT$, using the weight normal system; that is, the ratios are unity throughout, whereas all of the ratios at 20° and 10°, for the one solution studied, are above unity. These ratios, moreover, do not show a regular increase with increase in concentration, as do cane sugar solutions at the same temperatures.

If hydration be the cause for the excess of osmotic over gas pressure, it is, at 20°, independent of the concentration. Furthermore, the same excess of gas above osmotic pressure is found at 20° as at 10°, indicating that, if hydration be the cause of the excess pressure, this hydration is the same at 20° as at 10°. As is shown in the above table, the excess pressure disappears between 20° and 30°, which suggests that between these temperatures the "hydration" of glucose in aqueous solutions disappears.

BIOGRAPHY

Walter H. Coolidge was born December 13, 1890, at Cincinnati, Ohio. His early education was obtained in the public schools of that place, graduating in the spring of 1908. In the fall of that same year he entered Kenyon College, Gambier, Ohio, and graduated in 1912, receiving the degree of Bachelor of Philosophy. In 1912 he entered the graduate department of Johns Hopkins University, majoring in Chemistry with Physical Chemistry and Geology as his first and second subordinate subjects respectively. He was assistant in Chemistry at Kenyon College during the academic years 1909-'12.